

## Thermoluminescence Study of $\text{ZrO}_2\text{:Er}^{3+}, \text{Yb}^{3+}$

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### ABSTRACT

$\text{Er}^{3+}$ ,  $\text{Yb}^{3+}$  doped  $\text{ZrO}_2$  prepared by combustion method and characterized by XRD. Thermoluminescence glow curves of the prepared samples were recorded for UV radiation and their TL parameters was calculated. For the present sample we calculate the shape factor, order of kinetics, activation energy & frequency factor.

**Keywords:**  $\text{ZrO}_2\text{:Er}^{3+}, \text{Yb}^{3+}$ , Combustion synthesis, thermoluminescence.

### INTRODUCTION

Recently, interest has been increased in the application of nanoparticles in the design of photonic systems because of their luminescent properties and crystallite size<sup>1,2</sup>. It has been many years now that blue and green light sources are desirable for optical devices such as high density optical data storages, color displays, solid state lasers and sensors. Therefore, the upconversion of infrared light into visible light has been extensively studied on various crystals and glasses doped with rare-earth ions<sup>3-5</sup>. It has been reported that the  $\text{Yb}^{3+}$  ion is a very good sensitizer for the  $\text{Er}^{3+}$  upconversion emission under 980 nm excitation due to its high absorption cross section and the

resonance energy transfer to  $\text{Er}^{3+}$  ion<sup>6</sup>. Thermoluminescence is the emission of light from a solid either inorganic, semiconductor or an insulator when it is heated after its exposure to some radiation<sup>11</sup>. Thermoluminescence is one of the long investigated fields. Various aspects of TL have been theoretically as well as experimentally studied till date<sup>12-15</sup>. In case of UV irradiated phosphors the TL response mainly generates from the surface traps, since these radiations cannot penetrate deeper and hence will not induce lattice defects. The density of surface defects increases with increase in the UV exposure leading to increase in peak intensity. The fall in the TL intensity at higher doses has been reported earlier by several authors<sup>16,17</sup> and

usually a consequence of competition between radiative and nonradiative centre or between different kinds of trapping centers<sup>18</sup>.

## EXPERIMENTAL

### Sample Preparation

In this study Zirconium Nitrate (99.99% Sigma Aldrich) Erbium Nitrate (99.99% Sigma Aldrich) and Ytterbium Nitrate (99.99% Sigma Aldrich), Urea were used as starting raw material. To prepare  $\text{ZrO}_2:\text{Er}^{3+}$ ,  $\text{Yb}^{3+}$ , These  $\text{ZrO}_2(\text{NO}_3)_3$ ,  $\text{Er}(\text{NO}_3)_3$  and  $\text{Yb}(\text{NO}_3)_3$  were mixed according to the stoichiometry equation in a beaker and then a suitable amount of urea was added to prepare the precursor solution and kept stirring for 30 min. Finally this sample was transferred to crucible and fired in a furnace then water was evaporated quickly and soon a vigorous redox reaction occurred, the whole process went on for a few seconds at  $600^\circ\text{C}$ . Finally  $\text{ZrO}_2:\text{Er}^{3+}$ ,  $\text{Yb}^{3+}$

Nanophosphor with different concentration were obtained.

### Structural characterization

The morphologies and sizes of the rare earth doped  $\text{ZrO}_2$  were determined by X-ray diffraction studies with  $\text{Cu K}\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ). XRD data were collected over the range  $20^\circ$ - $80^\circ$  at room temperature. The X-ray diffraction patterns have been obtained data from X-ray Powder diffractometer. The particle size was determined using the sherrer's formula.

#### (i) TL READER:

For recording TL, samples were exposed to UV radiations from UVGL-58 handled UV lamp operating at 230V-50 Hz (emitting 253nm). TL glow curve were recorded on a TLD Reader (Model -1009I Made by nucleonix system private limited) fitted with photo-multiplier tube (PMT) by taking 5 mg of sample each time.

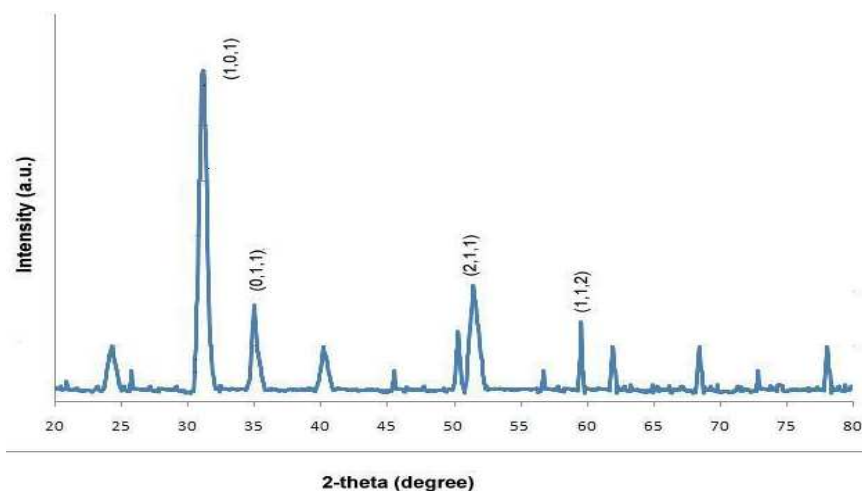


Fig1 Xrd result of  $\text{ZrO}_2:\text{Er}^{3+}$ ,  $\text{Yb}^{3+}$ , Nanophosphor

## RESULTS AND DISCUSSION

### 3.1. Structural characterization

The XRD patterns of  $\text{ZrO}_2: \text{Er}^{3+}, \text{Yb}^{3+}$  synthesis at  $600^\circ\text{C}$  temperature by combustion synthesis shown in Fig.1.

Four different peaks are obtained at  $2\theta$  values of  $31.17^\circ$ ,  $34.96^\circ$ ,  $51.45^\circ$  and  $59.53^\circ$ . and the peaks correspond to diffraction at (101), (011), (211) and (112) planes, respectively.

All diffraction patterns are in good agreement with JCPDS 37-1484. The size of the particles has been computed from the width of first peak using Debye Scherrer formula<sup>7</sup>.

$$D = 0.89\lambda / \beta \cos\theta$$

Where  $\lambda$  is the wavelength of the X-ray,  $\theta$  is the diffraction pattern angle and  $\beta$  is the corrected full width at half maximum

(FWHM) of the XRD peaks (corresponding to  $2\theta$ ). XRD techniques indicate that  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  doped  $\text{ZrO}_2$  nanophosphors have a mean size of 14 nm.

### (ii) TL RESULT

Thermoluminescence (TL) is a very sensitive technique for the detection of traps or defects<sup>8</sup>. Figure 2 shows the TL glow curve of  $\text{ZrO}_2: \text{Er}^{3+}, \text{Yb}^{3+}$  doped nanophosphor. The evaluation of kinetic parameter such as activation energy, order of kinetics and frequency factor was calculated by peak shape method. Shape factor  $\mu$  decide the order of kinetics of prepared sample its value is  $>0.42$  show the first order kinetics. One trap is present in the sample and the orders of kinetics decide the trap level of the sample. The activation energy is required energy from escaping one electron in the conduction band.

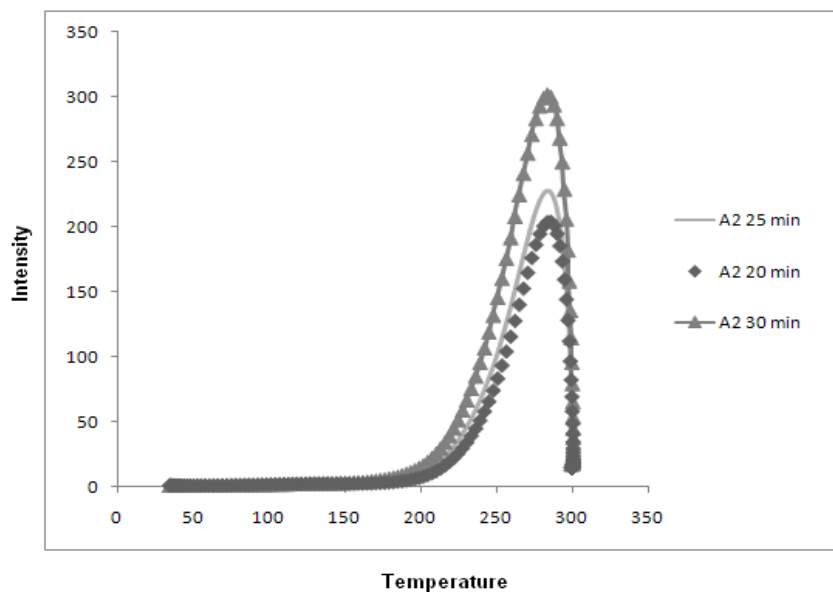


Fig 2 TL glow curve of  $\text{ZrO}_2: \text{Er}^{3+}, \text{Yb}^{3+}$ , with different UV exposure time

**Table 1 Kinetic Parameters of  $\text{ZrO}_2\text{:Er}^{3+}, \text{Yb}^{3+}$** 

Exp time (In Min)	$T_1$	$T_m$	$T_2$	$\tau = (T_m - T_1)$	$\delta = (T_2 - T_m)$	$\omega = (T_2 - T_1)$	$\mu = \delta/\omega$	Activation Energy E	Frequency factor S
20	529.15	558.44	571.32	29.29	12.88	42.17	0.30543	1.3429	$1.86 \times 10^{13}$
25	526.3	556.16	570.61	29.86	14.45	44.31	0.32611	1.3086	$1.0 \times 10^{13}$
30	523.44	556.16	570.61	32.72	14.45	47.17	0.30633	1.1877	$7.31 \times 10^{11}$

## CONCLUSION

The TL property of  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  doped  $\text{ZrO}_2$  nanophosphors has been investigated for UV irradiation. The trapping parameters were calculated. When the temperature is raised so that trapped electrons are thermally released from the shallower trap, these electrons may go either to the luminescence center or to the deeper trap.

In this TL glow curve  $\mu \approx 0.42$  or less than first order kinetics may be caused by the presence of one trap is present. The value of activation energy belongs to 1.18 eV to 1.34 eV and frequency factor  $3.2 \times 10^9$  to  $1.86 \times 10^{13}$ . The generation and analysis of TL spectra of luminescent materials carried out in this study show that the shape, intensity, and position of a glow curve can depend not only on the intrinsic parameters of the relevant trap but also on the presence of other traps, on the presence of preionized luminescence centers, and on the level of excitation used to create the TL spectrum. The study has highlighted a number of factors that may assist in the interpretation and understanding of

experimentally observed thermoluminescence spectra.

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